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Effect of zwitterions on electrochemical properties of oligoether-based electrolytes

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ABSTRACT

Solid polymer electrolytes show great potential in electrochemical devices. Poly(ethylene oxide) (PEO) has been studied as a matrix for solid polymer electrolytes because it has relatively high ionic conductivity. In order to investigate the effect of zwitterions on the electrochemical properties of poly(ethylene glycol) dimethyl ether (G5)/lithium bis(fluorosulfonyl) amide (LiFSA) electrolytes, a liquid zwitterion (ImZ2) was added to the G5-based electrolytes. In this study, G5, which is a small oligomer, was used as a model compound for PEO matrices. The thermal properties, ionic conductivity, and electrochemical stability of the electrolytes with ImZ2 were evaluated. The thermal stabilities of all the G5-based electrolytes with ImZ2 were above 150 °C, and the ionic conductivity values were in the range of 0.8–3.0 mS cm^{-1} at room temperature. When the electrolytes contained less than 5.5 wt% ImZ2, the ionic conductivity values were almost the same as that of the electrolyte without ImZ2. The electrochemical properties were improved with the incorporation of ImZ2. The anodic limit of the electrolyte with 5.5 wt% ImZ2 was 5.3 V vs. Li/Li$^+$, which was over 1 V higher than that of G5/LiFSA.

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1. Introduction

Polymer electrolytes have been investigated for their potential application in electrochemical devices, particularly in secondary lithium-ion batteries. Solid polymer electrolytes have several advantages, such as no leakage of electrolytes and no internal shorting. Poly(ethylene oxide) (PEO)/lithium salt complexes have been extensively studied as polymer electrolytes [1–7] because PEO has a high polarity, which promotes the dissociation of lithium salts, and high mobility, which can promote the transport of dissociated ions. However, the conductivity of these complexes is mainly due to the migration of anionic species; the lithium-ion transference number (t_{Li+}) is generally low, with values below 0.4. These low values may result in a concentration polarization that limits the rate (power) of batteries [8]. In addition, the anodic limit of pristine PEO is about 4.0 V. It is difficult to use electrodes with high charge voltages, such as LiCoO$_2$ and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC), as cathode materials [9,10]. In order to improve the electrochemical stability of these materials, many kinds of additives have been investigated. For example, PEO-based

electrolytes exhibited an anodic stability of up to 4.5 V with addition of low molecular weight poly(ethylene glycol) dimethyl ether (PEGDME) [11], ceramic fillers [12,13], or PEG-borate ester [14]. Although the electrochemical stability of PEO-based electrolytes was improved with these additives, the ionic conductivity values were below 10^{-4} S cm^{-1} at room temperature. It is still difficult to achieve high ionic conductivity and good electrochemical stability simultaneously because the additives cause an increase in the viscosity of matrices.

It has been reported that the addition of zwitterions promotes the dissociation of lithium salts and facilitates the transport of lithium ions in ionic-liquid-based electrolytes and polymer electrolytes [15]. In addition to enhancing the conduction of lithium ions, battery cycle performances were improved by the formation of a solid electrolyte interface (SEI) film on the surface of the electrodes [16–18]. We previously reported that an imidazolium-based zwitterion containing two oxyethylene units (ImZ2) can be synthesized as a colorless liquid at room temperature [19], and that lithium bis(fluorosulfonyl) amide (LiFSA) mixed with a small amount of the liquid zwitterion exhibited high ionic conductivity and t_{Li+} values [20].

In order to improve the lithium transference number and oxidation resistance at around 4.0 V for PEO, ImZ2 was added to poly(ethylene glycol) dimethyl ether (G5)/LiFSA electrolytes. In

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this study, we investigated the effects of ImZ2 on the ionic conductivity and electrochemical stability of G5/LiFSA electrolytes.

2. Experimental

2.1. Materials

3-(1-(2-Methoxyethoxyethyl)-1*H*-imidazol-3-ium-3-yl) propane-1-sulfonate (ImZ2) was synthesized according to the published procedure [19]. LiFSA (Piotrek, 99.0%) was used as received. Poly(ethylene glycol) dimethyl ether (G5) (Aldrich, M_n = 250) was dried *in vacuo* before use. The chemical structures of G5, LiFSA, and ImZ2 are shown in Fig. 1. G5 was mixed with LiFSA in an argon filled glove box. The molar ratio of ethylene oxide (EO) units to Li$^+$ was fixed at 20 for the G5/LiFSA electrolytes [21]. ImZ2 was then added to the G5/LiFSA electrolytes, and the resulting mixtures were stirred at 60 °C for 24 h to obtain G5/LiFSA/ImZ2(*x*), where *x* represents the content of ImZ2 in the electrolyte (*x* = 1.5, 5.5, 10, or 20 wt%). The water content in the G5/LiFSA/ImZ2(*x*) electrolytes was measured to be below 30 ppm using a Karl-Fisher moisture meter (756 KF Coulometer, Metrohm Co.).

2.2. Methods

Thermogravimetric analysis (TGA) was carried out on a TG-DTA instrument (TG-DTA7200, Hitachi High-Technologies Corp.) in a nitrogen gas atmosphere between 25 and 500 °C at a heating rate of 10 °C min^{-1}. The thermal behavior was studied by differential scanning calorimetry (DSC) (DSC7020, Hitachi High-Technologies Corp.) between -150 and 80 °C at a heating/cooling rate of 10 °C min^{-1}.

Density measurements were conducted using an Anton Paar DMA 38 density meter. Viscosity measurements were conducted using an Anton Paar AMVn automated microviscometer.

Ionic conductivity measurements were carried out using a locally designed cell made from two platinum electrodes. The cell constants were calculated with a 0.01 mol L^{-1} KCl aqueous solution. The ionic conductivity values were obtained by measuring the complex impedance between 5 and 1 MHz using an impedance analyzer (1260, Solatron) over the temperature range of -30 to 80 °C. The temperature was controlled using a constant temperature oven (SU-262, Espec Corp.).

Pulsed-field gradient NMR (PFG-NMR) diffusion measurements were performed on a Bruker 300 MHz UltraShield spectrometer with an Avance III console utilizing a Diff50 diffusion probe. The various constituents of the samples were measured using the ^{1}H nuclei for G5 and ImZ2, ^{19}F nuclei for the FSA anion, and ^{7}Li nuclei for the lithium cation. The experiments were performed using the stimulated spin-echo (STE) pulse sequence by varying the gradient in eight steps up to the maximum gradient strength [22]. This data was fit to the Stejskal-Tanner diffusion Eq. (1) [23] using the non-linear least-squares method. Samples were packed and sealed in 5 mm NMR tubes in an argon gas atmosphere. All measurements were conducted at 25 °C.

$$A = A_0 \exp[-(\gamma \delta G)^2 (\Delta - \delta/3) D] \tag{1}$$

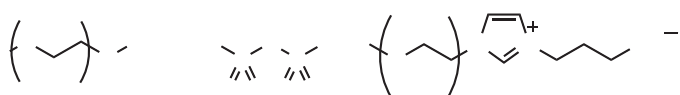where A_0 is the signal area without a gradient, γ is the gyromagnetic ratio of the nuclei under study, G is the gradient strength, Δ is the delay between the two gradients, δ is the duration of one of the gradient pulses, and D is the diffusion coefficient. For each measurement, the gradient pulse duration and diffusion time were typically 5 ms and 20 ms, respectively, and the gradient strength (G = 600–1400 G cm^{-1}) was optimized according to the diffusion coefficients.

The electrochemical stability of the electrolytes was evaluated by linear sweep voltammetry (LSV) at a sweep rate of 10 mV s^{-1} in the potential range of 0–6 V vs. Li/Li$^+$ at 25 °C. A stainless steel cell (TYS-00DM01, Toyo System Co., Ltd.) was used as the LSV measurement cell. A platinum plate polished with 1.0, 0.3, and 0.05 μm Al$_2$O$_3$ powder was used as the working electrode. A battery-grade lithium foil was used as the counter electrode. The measurements were performed using a potentiostat/galvanostat (HZ-7000, Hokuto Denko Co.).

The lithium plating/stripping performance of the Ni/electrolyte/Li cells was characterized using cyclic voltammetry (CV). A stainless steel cell (TYS-00DM01, Toyo System Co., Ltd.) was used as the CV measurement cell. A nickel plate polished with 1.0, 0.3, and 0.05 μm Al$_2$O$_3$ powder was used as the working electrode. A battery-grade lithium foil was used as the counter electrode. A separator film (Advantec GA-55) was soaked in the electrolytes before cell assembly. The cells were fabricated in an argon filled glove box. The CV measurements (scan rate: 10 mV s^{-1}) were performed between -0.25 and 1.0 V vs. Li/Li$^+$ using an electrochemical system (CH Instruments potentiostat/galvanostat, Model 660B).

3. Results and discussion

3.1. Thermal properties

TGA measurements were carried out for G5/LiFSA and G5/LiFSA/ImZ2(*x*). Watanabe and co-workers reported that complexes of glyme and lithium bis(trifluoromethylsulfonyl) amide (LiTFSA) are thermally stable up to 200 °C [24]. Although the onset thermal decomposition temperature (T_d) values of G5/LiFSA and G5/LiFSA/ImZ2(*x*) were about 150 °C, G5/LiFSA and G5/LiFSA/ImZ2(*x*) exhibited sufficient thermal stability (> 100 °C) for use as electrolytes in lithium-ion batteries. These lower T_d values could be due to low thermal stability of LiFSA compared with that of LiTFSA [20]. The DSC curves of the electrolytes are presented in Fig. 2. The G5/LiFSA and G5/LiFSA/ImZ2(*x*) electrolytes exhibited low glass transition temperatures (T_g) below -90 °C. In all the electrolytes
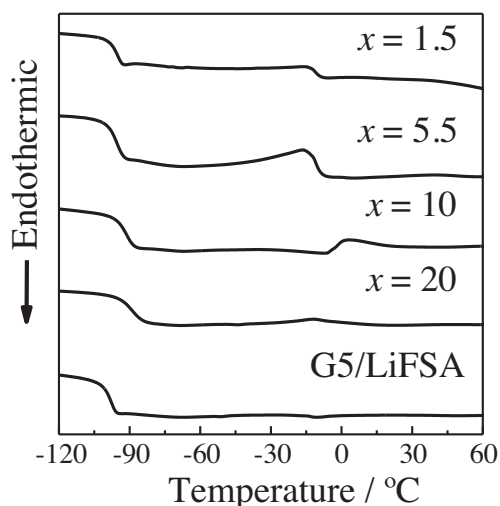
Fig. 1. Chemical structures of G5, LiFSA, and ImZ2.

Fig. 2. DSC curves of G5/LiFSA and G5/LiFSA/ImZ2(*x*).